

## RESEARCH REPORT

(to protect the scientific priority, only published results are presented here)

January 2015 – November 2015

### New Organometallic Compounds of Heavy Group 15 Metals (Antimony, Bismuth) -- Potential Use in Catalysis

PN-II-ID-PCE-2011-3-0933

In the phase 2015 of this project, besides current management activities (acquisition of reagents, solvents and other materials, small equipments), some of the studies started in the previous phases were completed, *i.e.*:

(i) the synthesis of organoantimony(III) and -bismuth(III) oxides, alkoxides and aryloxides containing a organic group with two pendant arms, *i.e.* 2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. All compounds were spectroscopically characterized in solution by multinuclear NMR (including studies at variable temperature), and in most cases the molecular structure was established by single-crystal X-ray diffraction. Hexamer clusters of water molecules with a [tetramer + 2] structure (two water molecules connected to the opposite corners of a square planar tetramer of water molecules) were evidenced for the first time in the crystal of the oxide [*ciclo-syn*-{2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>2</sub>Bi<sub>2</sub>O<sub>2</sub>·4H<sub>2</sub>O]<sub>n</sub>. Theoretical calculations were carried out in order to evaluate the stabilization energy due to the intramolecular coordination of the pendant arms, the degree of association and the formation energy of the studied organopnicogen compounds. The results were reported in an article published in the prestigious journal *Dalton Transactions*.<sup>1</sup>

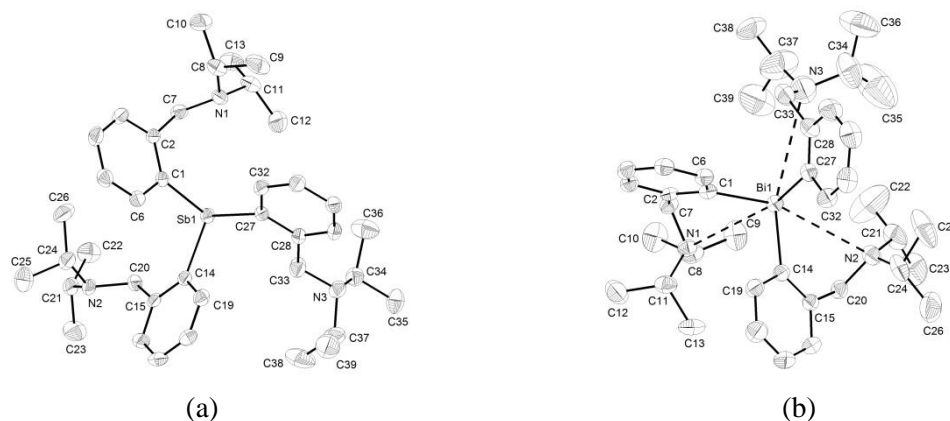
(ii) phenols with a terphenyl backbone, 2,4,6-R<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH [R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, Me<sub>5</sub>C<sub>6</sub>], which will be used in the synthesis of organopnicogen derivatives. The results obtained are the subject of an article published in the journal *Z. Naturforsch., B: Chem. Sci.*<sup>2</sup>

(iii) ionic compounds with diorganoantimony(III) cations stabilized through intramolecular coordination and their conversion to diorganoantimony(III) fluorides; the preparation method of these fluorides is an original and general one, at least in the case of compounds containing an organic group with a pendant arm capable of intramolecular coordination. The results obtained are the subject of an article published in the journal *RSC Advances*.<sup>3</sup>

(iv) new organic proligands with a chiral nitrogen atom, *i.e.* 2-(MesNHCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br, 2-[Mes(Me)NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br and 2-[Mes{(O)CH}NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br, which can be utilized for the preparation of chiral organometallic species. The compounds were characterized by multinuclear NMR and IR spectroscopy, and mass spectrometry. The molecular structure of 2-[Mes{(O)CH}NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br was established by single-crystal X-ray diffraction. The results obtained are the subject of an article published in the journal *Revue Roumaine de Chimie*.<sup>4</sup>

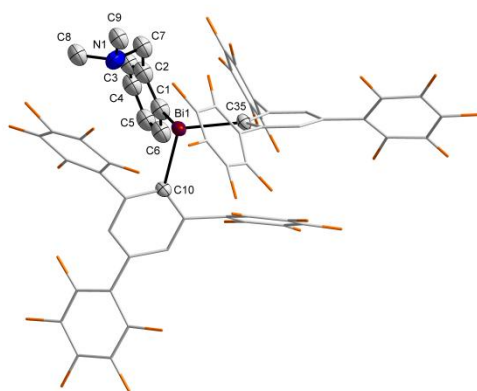
(v) two new homoleptic triorganopnicogen(III) derivatives, [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>M (M = Sb, Bi), obtained by reacting [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]MgBr (prepared *in situ* from [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]Br and Mg) with MCl<sub>3</sub>. The compounds were characterized by multinuclear NMR spectroscopy in solution and single-crystal X-ray diffraction. The NMR data in solution are consistent with equivalent organic substituents attached to the metal atom, while in solid state there are significant differences: the pendant arms in the antimony derivative are twisted to push the nitrogen atoms far from the central atom (Figure 1a), while in the bismuth analogue there are weak N→Bi

intramolecular interactions (Figure 1b), resulting in a distorted octahedral coordination geometry in the (C,N)<sub>3</sub>Bi core. The results obtained are the subject of an article published in the journal *Revue Roumaine de Chimie*.<sup>5</sup>



**Figure 1.** Molecular structure of the compounds (a) [2-(*i*Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Sb, and (b) [2-(*i*Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi.

The studies on the chiral derivatives with fluoro-organic groups attached to a bismuth atom were extended with the synthesis of the compound [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>][2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>Bi, obtained by reacting [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> and 2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li, in 1:2 molar ratio. The compound was characterized by multinuclear NMR spectroscopy in solution and single-crystal X-ray diffraction (Figure 2).



**Figure 2.** Molecular structure of the compound [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>][2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>Bi.

In contrast to [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>](C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Bi, which is sensitive to oxygen and moisture, the compound [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>][2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>Bi is stable to air and water, in spite of the presence of an electron deficient organic groups. This behavior is due to the increased kinetic stability as result of the steric protection offered by terphenyl substituents. This protection is also suggested by the <sup>13</sup>C and <sup>19</sup>F NMR spectra which indicate that the free rotation of the C<sub>6</sub>F<sub>5</sub> groups in the positions 2 and 6 of the terphenyl ligand is blocked. The results obtained in the study of the chiral species with C<sub>6</sub>F<sub>5</sub> groups attached to a bismuth atom are the subject of a manuscript submitted for publication in December 2015.<sup>6</sup>

The research studies developed in collaboration with the group of Prof. Ulrich Körtz (Jacobs Universität, Bremen, Germany) were continued; new ionic compounds with a discrete heteropolywolframate anion incorporating one, two or three PhSb(III) or [2-(Me<sub>2</sub>HN<sup>+</sup>CH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]Sb(III) fragments, were obtained. The compounds were characterized by multinuclear NMR spectroscopy in solution, IR spectroscopy and single-crystal X-ray diffraction. The *in vitro* inhibitory activity towards various kinds of bacteria was investigated; the activity was proved to increase with the number of the organoantimony(III) groups incorporated into the

heteropolywolframate anion. The results obtained are the subject of an article published in the prestigious journal *Chemistry – A European Journal*,<sup>7</sup> and of a second one *in press* in *Inorganic Chemistry*.<sup>8</sup>

### Studies on the catalytic activity of some organopnicogen(III) compounds

New monoorganoantimony(III) alkoxides and aryloxides, with organic groups containing one pendant arm capable for intramolecular coordination, were prepared. They were isolated as white solids, stable in air at room temperature. The identity of the compounds was confirmed by multinuclear NMR spectroscopy in solution and the molecular structure of some representative compounds was established by single-crystal X-ray diffraction. Dimer associations through O→Sb intermolecular interactions were observed in the crystal of such compounds; the metal centre becomes pentacoordinated, with a distorted trigonal bipyramidal geometry.

These compounds will be tested for their reactivity towards CO<sub>2</sub> as well as their catalytic properties in various reactions. The studies performed so far within this project on the catalytic activity of the obtained organoantimony(III) and – bismuth(III) compounds for the synthesis of cyclic carbonates and/or polycarbonates from CO<sub>2</sub> were not conclusive.

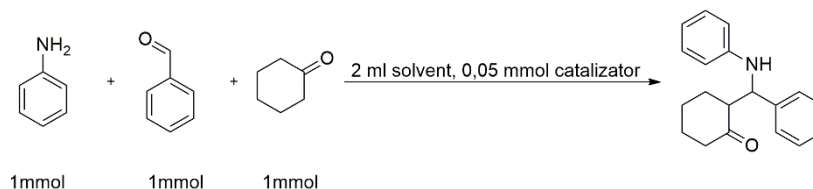
The studies regarding the catalytic properties of some cationic, hypervalent organoantimony(III) compounds for the “one-pot” Mannich reaction were continued. Two main objectives were considered, *i.e.* the generation of some stable diorganoantimony(III) cations and the screening of their catalytic properties.

#### (i) *Generation of diorganoantimony(III) cations*

The organoantimony(III) cations can be obtained by reacting an organoantimony(III) halide with the salt of an anion with weak coordination properties as, for example Ag[SbF<sub>6</sub>], Tl[PF<sub>6</sub>], Ag[BF<sub>4</sub>], Na[BAr<sup>F</sup><sub>4</sub>]; Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Several attempts were carried out and after the separation of the insoluble silver(I) or thallium(I) halides, the obtained new organoantimony(III) species were characterized by multinuclear (<sup>1</sup>H, <sup>19</sup>F) NMR spectroscopy in solution. In some cases the nature of the organometallic products obtained are still under investigation.

#### (ii) *Studies on the catalytic effect of diorganostibiu(III) cations on Mannich reactions*

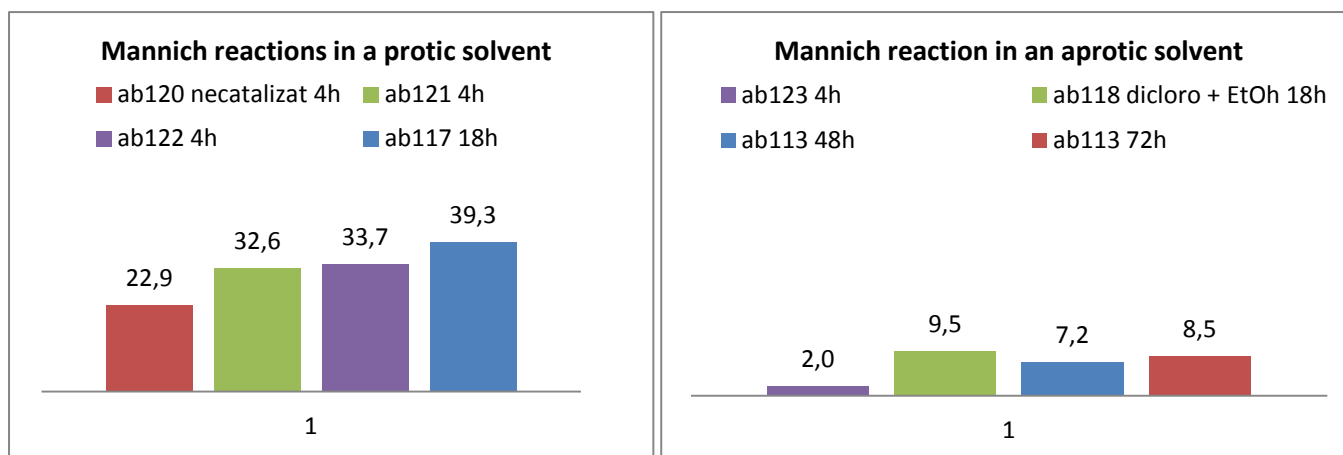
The catalytic screenings were performed for a typical Mannich reaction between aniline, benzaldehyde and cyclohexanone in 1:1:1 molar ratio (Scheme 1), using a certain amount of catalyst, in various solvents, at room temperature.



**Scheme 1**

The reactions were monitored for 4 hours by chromatography, followed by the work-up of the reaction mixture. The crude products were analyzed by GC/MS, after the separation of the catalyst. The best results were obtained using a protic solvent (Chart 1). The screened compounds proved to be useful for the formation of a C-C bond in the tested system.

**Chart 1** Yields of a Mannich reaction catalyzed by a ionic diorganoantimony(III) compound in a protic and an aprotic solvent



### Transition metal complexes with triorganostibines – potential catalysts in coupling reactions

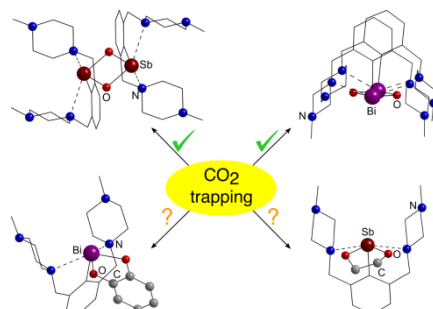
Several new Cu(I) and Pd(II) complexes with carbenes and triorganostibines were prepared in order to perform their screening as catalysts in coupling reactions. The Cu(I) and Pd(II) complexes with carbenes were isolated as white and yellow solids, respectively. They were used as starting materials for new complexes containing triorganostibines. Ionic Cu(I) and neutral Pd(II) complexes containing both carbene and  $R_3Sb$  as ligands were isolated. During the next phases of the project the potential catalytic activity of some of the obtained transition metal complexes will be screened in coupling reactions.

Complexes of palladium with bulky isocyanide ligands as 2,4,6-Mes<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NC and 2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NC were prepared and structurally characterized by NMR spectroscopy in solution, IR spectroscopy, mass spectrometry, and the molecular structure of two representative complexes was established by single-crystal X-ray diffraction. These complexes can be used further as starting materials for the preparation of complexes containing triorganostibines, with potential use as catalysts. Part of the obtained results were presented within the conference *Zilele Academice Iesene - A XXV-a Sesiune de Comunicări Stiintifice a Institutului de Chimie Macromoleculară „Petru Poni”*, Iasi, September 24-26, 2015 (*Palladium Coordination Compounds with Bulky Isocyanide Ligands*, K. T. Kegyes, M. Olaru, C. Silvestru, C. I. Rat).

## References

1. **A general route to monoorganopnicogen(III) (M = Sb, Bi) compounds with a pincer (N,C,N) group and oxo ligands,**

G. Strimb, A. Pöllnitz, C. I. Raț and C. Silvestru,  
*Dalton Trans.*, **2015**, 44, 9927-9942.  
 DOI: 10.1039/c5dt00603a



The reaction of  $\text{RMCl}_2$  [ $\text{R} = 2,6\text{-}[\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2]_2\text{C}_6\text{H}_3$ ;  $\text{M} = \text{Sb}$  (**1**),  $\text{Bi}$  (**2**)] with  $\text{KOH}$  affords the isolation of the oxides  $\text{cyclo-R}_2\text{M}_2\text{O}_2$  [ $\text{M} = \text{Sb}$  (**3**),  $\text{Bi}$  (**4**)]. Treatment of **3** with trifluoroacetic acid produced an ionic species (**5**) with a dinuclear cation that contains organic ligands protonated partially at one of the pendant arms. The cyclic oxides **3** and **4** are able to trap gaseous  $\text{CO}_2$  to give "RMCO<sub>3</sub>" [ $\text{M} = \text{Sb}$  (**6**),  $\text{Bi}$  (**7**)], the degree of these organometallic carbonates' oligomerization being under investigation. The reactivity of the dinuclear oxide **3** was also investigated towards oxalic acid or dopamine hydrochloride and pure mononuclear compounds could be isolated, *i.e.*  $\text{RSb}[\text{O}(\text{O})\text{CC}(\text{O})\text{O}]$  (**8**) and  $\text{RSb}[\text{O}_2\text{-}1,2\text{-C}_6\text{H}_3\text{-}3\text{-(CH}_2)_2\text{NH}_3]\text{Cl}$  (**9**). The reaction of the dichlorides **1** and **2** with ethylene glycol, pinacol or catechol, in the presence of  $\text{KOH}$ , led to 2-organo-1,3,2-dioxastibolanes or -bismolanes  $\text{RM}(\text{OCH}_2)_2$  [ $\text{M} = \text{Sb}$  (**10**),  $\text{Bi}$  (**11**)],  $\text{RM}(\text{OCMe}_2)_2$  [ $\text{M} = \text{Sb}$  (**12**),  $\text{Bi}$  (**13**)] and 2-organo-1,3,2-dioxastibole or -bismole  $\text{RM}(\text{O}_2\text{-}1,2\text{-C}_6\text{H}_4)$  [ $\text{M} = \text{Sb}$  (**14**),  $\text{Bi}$  (**15**)], respectively. The compounds were investigated by NMR spectroscopy, including variable temperature experiments, providing evidence for the presence of the intramolecular  $\text{N} \rightarrow \text{M}$  interactions in solution. Single crystal X-ray diffraction studies were performed for most compounds and revealed an organic group  $\text{R}$  acting as a pincer ligand resulting in a distorted square pyramidal  $(\text{N,C,N})\text{MO}_2$  core with *cis* intramolecular  $\text{N} \rightarrow \text{M}$  interactions placed *trans* to  $\text{M}-\text{O}$  bonds. This is in contrast to the  $\text{N} \rightarrow \text{M}$  interactions *trans* to each other as found in the  $\text{RMCl}_2$  used as starting materials. The crystals of the oxides **3** and **4**· $4\text{H}_2\text{O}$  contain different geometric isomers with *anti* and *syn* orientation of the  $\text{M}-\text{C}$  bonds, respectively, with respect to the planar  $\text{M}_2\text{O}_2$  ring. In the supramolecular polymeric architecture established in the crystal of **4**· $4\text{H}_2\text{O}$  an important finding is the experimental observation of water hexamer units with a [tetramer + 2] structure (water molecules connected to opposite corners of a square water tetramer) fixed between 1D-chains of the type  $(\text{syn-R}_2\text{Bi}_2\text{O}_2 \cdot \text{H}_2\text{O})_n$  through additional hydrogen bonds to oxygen atoms of the dinuclear organobismuth(III) moieties. Theoretical calculations were carried out on **2–6** and **8–15** in order to gain insight into the stabilization energy produced by intramolecular coordination of the pendant arms, association degrees and formation energies of the organopnicogen compounds with chelating ligands.

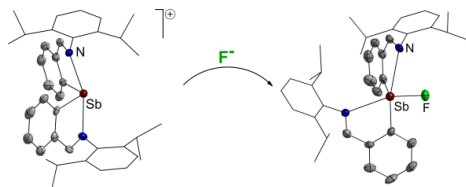
2. **Synthesis and structural characterization of substituted phenols with *m*-terphenyl backbone, 2,4,6- $\text{R}_3\text{C}_6\text{H}_2\text{OH}$  ( $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ,  $\text{Me}_5\text{C}_6$ ),**

A. B. Solea, M. Olaru, C. Silvestru and C. I. Raț,  
*Z. Naturforsch., B: Chem. Sci.*, **2015**, 70, 77-81.  
 DOI: 10.1515/znb-2014-0180

**Abstract:** Substituted phenols with a *m*-terphenyl backbone 2,4,6- $\text{R}_3\text{C}_6\text{H}_2\text{OH}$  [ $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$  (**1**),  $\text{Me}_5\text{C}_6$  (**2**)] were synthesized using Kumada cross-coupling reactions between 2,4,6- $\text{I}_3\text{C}_6\text{H}_2\text{OH}$  and the corresponding Grignard reagent. Both compounds were structurally characterized in solution by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and HRMS. The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction.

3. **Hypervalent diorganoantimony(III) fluorides via diorganoantimony(III) cations – a general method of synthesis,**

A. M. Preda, C. I. Raț, C. Silvestru, H. Lang, T. Rüffer and M Mehring,  
*RSC Advances*, **2015**, 5, 99832-99840.  
 DOI: 10.1039/c5ra21788a

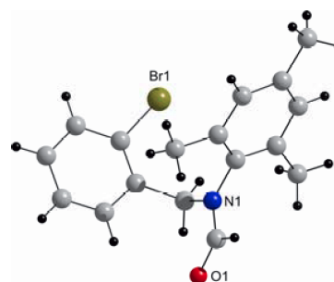


Novel diorganoantimony(III) fluorides containing ligands with pendant arms,  $R_2SbF$  (5),  $(R)PhSbF$  (6) [ $R = 2-(2',6'-Pr_2C_6H_3N=CH)C_6H_4$ ],  $R''_2SbF$  (7) and  $(R'')PhSbF$  (8) [ $R'' = 2-(Me_2NCH_2)C_6H_4$ ], were prepared via the ionic derivatives  $[R_2Sb]^+[PF_6]^-$  (1),  $[(R)PhSb]^+[PF_6]^-$  (2),  $[R''_2Sb]^+[SbF_6]^-$  (4) and  $[(R'')PhSb]^+[SbF_6]^-$  (obtained *in situ*) by treatment with  $[Bu_4N]F \cdot 3H_2O$ . The ionic species used as starting materials as well as  $[R'_2Sb]^+[PF_6]^-$  (3) [ $R' = 2-(2',4',6'-Me_3C_6H_2N=CH)C_6H_4$ ] were obtained from the corresponding bromides or chlorides and  $Tl[PF_6]$  or  $Ag[SbF_6]$ . The compounds were investigated by multinuclear NMR spectroscopy in solution, MS and IR spectroscopy in the solid state. The molecular structures of the ionic species  $1 \cdot 2CH_2Cl_2$  and  $3 \cdot 2CHCl_3$  as well as of the fluorides 5–8 were determined by single-crystal X-ray diffraction.

4. **Synthesis and characterization of 2-[Mes(Me)NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br and 2-[Mes{(O)CH}NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br – Precursors for novel one pendant arm ligands,**

G. Strimb, C. I. Rat and C. Silvestru,  
*Rev. Roum. Chim.*, **2015**, 60, 651-657.

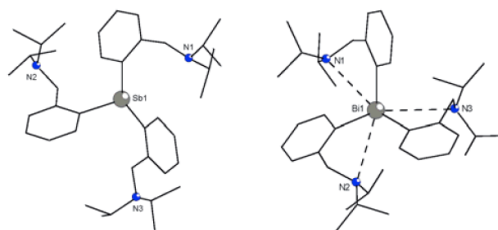
A new secondary amine 2-(MesNHCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br (**2**) was synthesized starting from imine 2-(MesN=CH)C<sub>6</sub>H<sub>4</sub>Br (**1**) and NaBH<sub>4</sub>. Reaction of **2** with paraformaldehyde and HC(O)OH gave almost quantitatively 2-[Mes(Me)NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br (**3**), while treatment of **2** with paraformaldehyde and CH<sub>3</sub>C(O)OH resulted in **3** as a major product besides a minor amount of the unexpected 2-[Mes{(O)CH}NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br (**4**) compound. The compounds were characterized by multinuclear NMR and IR spectroscopy, mass spectrometry and the molecular structure of **4** was established by single-crystal X-ray diffraction.



5. **Homoleptic organometallic compounds of heavy pnicogens. Crystal and molecular structure of [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>M (M = Sb, Bi),**

I. Chirca, A. Soran, A. Silvestru and C. Silvestru,  
*Rev. Roum. Chim.*, **2015**, 60, 643-650.

Two new homoleptic triorganopnicogen(III) species,  $[2-(^iPr_2NCH_2)C_6H_4]_3M$  [ $M = Sb$  (**2**),  $Bi$  (**3**)] were obtained by reacting  $[2-(^iPr_2NCH_2)C_6H_4]MgBr$  (prepared *in situ* from  $[2-(^iPr_2NCH_2)C_6H_4]Br$  (**1**) and  $Mg$  filings) with  $MCl_3$ . The compounds were characterized by multinuclear NMR solution studies and the crystal and molecular structure of **2** and **3** was established by single-crystal X-ray diffraction. The NMR data are consistent with one type of organic group attached to the metal atom in **2** and **3**. The main difference between the molecules of the organometallic species is observed in the solid state. While for the antimony(III) compound all pendant arms are twisted to push the nitrogen atoms far from the metal centre, in the bismuth(III) derivative weak intramolecular  $N \rightarrow Bi$  interactions are established for all three nitrogen atoms, thus increasing the coordination number from three to six in a distorted octahedral  $(C,N)_3Bi$  core.



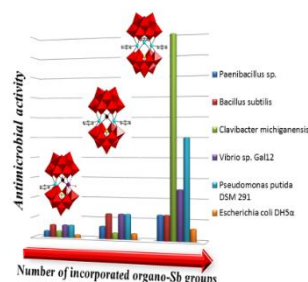
6. **Mixed triorganobismuthines  $RR'_2Bi$  [ $R' = C_6F_5$ , 2,4,6-( $C_6F_5$ )<sub>3</sub>C<sub>6</sub>H<sub>2</sub>] and hypervalent racemic Bi-chiral diorganobismuth bromides  $RR'BiBr$  ( $R' = C_6F_5$ , Mes, Ph) with the pendant arm ligand  $R = 2-(Me_2NCH_2)C_6H_4$ . Influences of the organic substituent,**

M. Olaru, M. Nema, A. Soran, H. J. Breunig and C. Silvestru,  
**2015**, *submitted*.

**Abstract:** Triorganobismuthines  $R(C_6F_5)_2Bi$  (**1**) and  $R[2,4,6-(C_6F_5)_3C_6H_2]_2Bi$  (**2**) [ $R = 2-(Me_2NCH_2)C_6H_4$ ] were synthesized by reaction of  $RBiBr_2$  with  $C_6F_5MgBr$ , and 2,4,6-( $C_6F_5$ )<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li, respectively, in 1:2 molar ratio. The Bi-chiral bromides  $R(C_6F_5)_2BiBr$  (**3**),  $R(Mes)BiBr$  (**4**), and  $R(Ph)BiBr$  (**5**) were obtained from  $RBiBr_2$  and  $C_6F_5MgBr$ ,  $MesMgBr$  or  $PhMgBr$ , or from  $PhBiBr_2$  and RLi, in 1:1 molar ratio. The molecular structures of **1–5** determined by single-crystal X-ray diffraction are discussed. The <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectroscopic features of **1–5** and their solution behavior are also detailed.



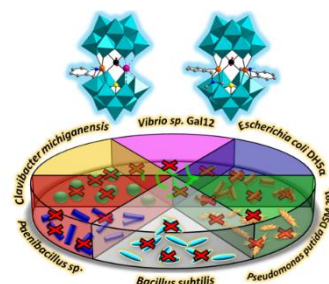
7. **Organoantimony(III)-containing tungstoarsenates(III): from controlled assembly to biological activity,**  
P. Yang, B. S. Bassil, Z. Lin, A. Haider, G. Alfaro-Espinoza, M. S. Ullrich, C. Silvestru and U. Kortz,  
*Chem. Eur. J.*, **2015**, *21*, 15600-15606.  
DOI: 10.1002/chem.201502398



**Abstract:** A family of three sandwich-type, phenylantimony(III)-containing tungstoarsenates(III),  $[(\text{PhSb}^{\text{III}})\{\text{Na}(\text{H}_2\text{O})\}\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{11-}$  (**1**),  $[(\text{PhSb}^{\text{III}})_2\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{10-}$  (**2**), and  $[(\text{PhSb}^{\text{III}})_3(\beta\text{-}\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{12-}$  (**3**), have been synthesized by one-pot procedures and isolated as hydrated alkali metal salts,  $\text{Cs}_3\text{K}_{3.5}\text{Na}_{4.5}[(\text{PhSb}^{\text{III}})\{\text{Na}(\text{H}_2\text{O})\}\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 41\text{H}_2\text{O}$  (**CsKNa-1**),  $\text{Cs}_{4.5}\text{K}_{5.5}[(\text{PhSb}^{\text{III}})_2\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 35\text{H}_2\text{O}$  (**CsK-2**), and  $\text{Cs}_{4.5}\text{Na}_{7.5}[(\text{PhSb}^{\text{III}})_3(\beta\text{-}\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2]\cdot 42\text{H}_2\text{O}$  (**CsNa-3**). The number of incorporated  $\{\text{PhSb}^{\text{III}}\}$  units could be selectively

tuned from one to three by careful control of the reaction parameters. The three compounds were characterized in the solid state by single-crystal XRD, IR spectroscopy, and thermogravimetric analysis. The aqueous solution stability of sandwich polyanions **1–3** was also studied by multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{183}\text{W}$ ) NMR spectroscopy. Effective inhibitory activity against six different kinds of bacteria was identified for all three polyanions, for which the activity increased with the number of incorporated  $\{\text{PhSb}^{\text{III}}\}$  groups.

8. **19-Tungstodiarсенate(III) functionalized by organoantimony(III) groups: tuning the structure-bioactivity relationship,**  
P. Yang, Z. Lin, G. Alfaro-Espinoza, M. S. Ullrich, C. I. Raț, C. Silvestru and U. Kortz,  
*Inorg. Chem.*, **2015**, *in press*.  
DOI: 10.1021/acs.inorgchem.5b02189



**Abstract:** A family of three discrete organoantimony(III)-functionalized heteropolyanions,  $[\text{Na}\{2\text{-(Me}_2\text{HN}^+\text{CH}_2\text{)C}_6\text{H}_4\text{Sb}^{\text{III}}\}\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})\}^{10-}$  (**1**),  $[\{2\text{-(Me}_2\text{HN}^+\text{CH}_2\text{)C}_6\text{H}_4\text{Sb}^{\text{III}}\}_2\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})\}^{8-}$  (**2**), and  $[\{2\text{-(Me}_2\text{HN}^+\text{CH}_2\text{)C}_6\text{H}_4\text{Sb}^{\text{III}}\}\{\text{WO}_2(\text{H}_2\text{O})\}\{\text{WO}(\text{H}_2\text{O})\}_2(\beta\text{-}\alpha\text{-As}^{\text{III}}\text{W}_8\text{O}_{30})(\beta\text{-}\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2\}^{14-}$  (**3**), have been prepared by one-pot reactions of the 19-tungstodiarсенate(III) precursor  $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$  with  $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{SbCl}_2$ . The three novel polyanions crystallized as the hydrated mixed-alkali salts  $\text{Cs}_3\text{KNa}_6[\text{Na}\{2\text{-(Me}_2\text{HN}^+\text{CH}_2\text{)C}_6\text{H}_4\text{Sb}^{\text{III}}\}\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 43\text{H}_2\text{O}$  (**CsKNa-1**),  $\text{Rb}_{2.5}\text{K}_{5.5}[\{2\text{-(Me}_2\text{HN}^+\text{CH}_2\text{)C}_6\text{H}_4\text{Sb}^{\text{III}}\}_2\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 18\text{H}_2\text{O}\cdot \text{Me}_2\text{NCH}_2\text{C}_6\text{H}_5$  (**RbK-2**), and  $\text{Rb}_{2.5}\text{K}_{11.5}[\{2\text{-(Me}_2\text{HN}^+\text{CH}_2\text{)C}_6\text{H}_4\text{Sb}^{\text{III}}\}\{\text{WO}_2(\text{H}_2\text{O})\}\{\text{WO}(\text{H}_2\text{O})\}_2(\beta\text{-}\alpha\text{-As}^{\text{III}}\text{W}_8\text{O}_{30})(\beta\text{-}\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2]\cdot 52\text{H}_2\text{O}$  (**RbK-3**), respectively. The number of incorporated  $\{2\text{-(Me}_2\text{HN}^+\text{CH}_2\text{)C}_6\text{H}_4\text{Sb}^{\text{III}}\}$  units could be tuned by careful control of the experimental parameters. Polyanions **1** and **2** possess a dimeric sandwich-type topology, whereas **3** features a trimeric, wheel-shaped structure, representing the largest organoantimony-containing polyanion. All three compounds were fully characterized in the solid state by single-crystal XRD, IR spectroscopy, and thermogravimetric analysis, and their aqueous solution stability was validated by UV-vis and multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{183}\text{W}$ ) NMR spectroscopy. Effective inhibition against six different kinds of bacteria was observed for **1** and **2**, and we could extract a structure-bioactivity relationship for these polyanions.

Project Director,  
**Prof. Dr. Cristian Silvestru**

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